

# For Reference

---

**NOT TO BE TAKEN FROM THIS ROOM**

# For Reference

---

NOT TO BE TAKEN FROM THIS ROOM

Ex libris  
UNIVERSITATIS  
ALBERTAENSIS



## Regulations Regarding Theses and Dissertations

[illegible]



THE UNIVERSITY OF ALBERTA

ELECTROCHEMISTRY OF GROUP IIB METAL IONS  
IN MOLTEN  $\text{AlCl}_3$ - $\text{NaCl}$ - $\text{KCl}$  EUTECTIC

BY



D. A. HAMES

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE  
OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

DECEMBER, 1967.



UNIVERSITY OF ALBERTA  
FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read,  
and recommend to the Faculty of Graduate Studies for  
acceptance, a thesis entitled

ELECTROCHEMISTRY OF GROUP IIB METAL IONS IN  
MOLTEN  $\text{AlCl}_3$ -NaCl-KCl EUTECTIC


submitted by D. A. Hames in partial fulfilment of the  
requirements for the degree of Master of Science in





ABSTRACT

The existence of two oxidation states of cadmium in molten  $\text{AlCl}_3\text{-NaCl-KCl}$  at  $150^\circ\text{C}$  is illustrated by the electroanalytical techniques of potentiometry, voltammetry, and chronopotentiometry. The relationship of Berzins and Delahay, relating the transition time for the second electrochemical step in a multiple step oxidation or reduction to the transition time for the first electrochemical step, was obeyed for the successive reduction of  $\text{CdCl}_2$  dissolved in this eutectic. Diffusion coefficients of  $\text{Zn(II)}$ ,  $\text{Cd(II)}$ , and  $\text{Cd(I)}$  were calculated from chronopotentiometric data, and standard potentials were determined for couples involving the Group II metal ions as well as for the  $\text{Ag(I)/Ag(0)}$  couple. Equilibrium constants were obtained for the reaction of the divalent cations of mercury and cadmium with their respective metals.



Digitized by the Internet Archive  
in 2019 with funding from  
University of Alberta Libraries

<https://archive.org/details/Hames1968>

ACKNOWLEDGEMENTS

The author wishes to thank Dr. J. A. Plambeck for his guidance and encouragement.

Financial assistance from the University of Alberta and the National Research Council is gratefully acknowledged.



TABLE OF CONTENTS

Abstract.....	iii
Acknowledgements.....	iv
List of Tables.....	vi
List of Figures.....	vii
List of Symbols.....	viii
I. INTRODUCTION	
I-1 The Ternary Eutectic $\text{AlCl}_3$ - $\text{NaCl}$ - $\text{KCl}$ .....	1
I-2 The $\text{Cd}$ - $\text{CdCl}_2$ System.....	2
I-3 Acid Stabilization of Lower Valence States.....	4
I-4 Solutions of $\text{CdCl}_2$ in Molten $\text{NaAlCl}_4$ .....	5
II. EXPERIMENTAL	
II-1 Reagents.....	9
II-2 Apparatus.....	12
II-3 The $\text{Al(III)}/\text{Al(0)}$ Reference Electrode...	13
III. RESULTS AND DISCUSSION	
III-1 Potential Measurements.....	16
III-2 Voltammetric Measurements.....	22
III-3 Chronopotentiometric Measurements.....	26
IV. CONCLUSION.....	46
V. BIBLIOGRAPHY.....	48



LIST OF TABLES

Table		Page
1.	The Number of Electrons Involved in the Reduction of Certain Metal- Metal Halide and Metal Halide- NaAlCl <sub>4</sub> Solutions .....	3
2.	The Percentage Reduction of Cd(II) by Metallic Cadmium in the Melts CdX <sub>2</sub> and CdX <sub>2</sub> -2AlX <sub>3</sub> .....	7
3.	The Determination of the Standard Potential for the Hg(I)/Hg(O) Couple in Molten AlCl <sub>3</sub> -NaCl-KCl.....	19
4.	An Electromotive Force Series in Molten AlCl <sub>3</sub> -NaCl-KCl.....	20
5.	A Comparison of Standard Potential Values Obtained in this Study with Values From Other Studies.....	23
6.	Chronopotentiometric Results Obtained for Solutions of CdCl <sub>2</sub> In Molten AlCl <sub>3</sub> -NaCl-KCl.....	35





LIST OF FIGURES

Figure		Page
1.	Electrolytic Cell .....	11
2.	Polarization Study on the Aluminum Reference Electrode. Potentials are Measured With Respect to the Ag(I)/Ag(O) Reference Electrode .....	15
3.	Voltammetric Scans for Dilute Solutions of Metal Chlorides at a Tungsten Cylinder Electrode.....	25
4.	Chronopotentiogram for a Dilute ZnCl <sub>2</sub> Solution.....	29
5.	The Effect of Reciprocal Current Density on the $\tau^{1/2}/C$ Ratio for Dilute ZnCl <sub>2</sub> Solutions .....	31
6A.	Chronopotentiogram for a Dilute CdCl <sub>2</sub> Solution.....	32
6B.	Chronopotentiogram for the Oxidation of Cadmium Metal.....	32
7.	The Effect of Reciprocal Current Density on the $\tau^{1/2}/C$ Ratio for Dilute CdCl <sub>2</sub> Solutions .....	36
8.	Chronopotentiogram for a Dilute HgCl <sub>2</sub> Solution .....	41



LIST OF SYMBOLS

A	Electrode area
C	Concentration
d	Density
D	Diffusion coefficient
E.A.	Electron affinity
$E^{\circ}$	Standard potential
$E_{1/2}$	Half-wave potential
$E_{\tau/4}$	Potential at one-quarter transition time
f	Activity coefficient
F	Faraday
i	Current
I.P.	First ionization potential
M	Molarity
m	Molality
n	Faradays per molar unit of reaction
o	Oxidant
r	Reductant
R	Gas constant
t	Celsius temperature



$T$	Absolute temperature
$U_o$	Lattice energy
$X$	Mole fraction
$\Delta H_f$	Heat of formation
$\Delta H_v$	Heat of vaporization
$\Delta H_D$	Heat of dissociation
$\tau$	Transition time



## I. INTRODUCTION

This study is concerned with E.M.F., voltammetric, and chronopotentiometric measurements of the group IIB metal ions in an  $\text{AlCl}_3$ -NaCl-KCl eutectic and was initiated by interest in the existence of a subvalent state of cadmium. The divalent oxidation state of cadmium is the most common and standard potentials have been assigned to the  $\text{Cd(II)}/\text{Cd(0)}$  couple in several molten salts<sup>1</sup> although no potential values have been assigned to couples such as  $\text{Cd(II)}/\text{Cd(I)}$  or to  $\text{Cd(I)}/\text{Cd(0)}$ .

### I-1. The Ternary Eutectic $\text{AlCl}_3$ -NaCl-KCl

The ternary eutectic used in this study (66 mole %  $\text{AlCl}_3$ , 20 mole % NaCl and 14 mole % KCl) has an unusually low melting point of  $70^\circ\text{C}$ <sup>2,3,4</sup> as compared to the considerably higher melting points of most molten salts. The eutectic is a good conductor of electricity and it has a specific conductivity of  $0.365$  to  $0.118 \Omega^{-1} \text{cm}^{-1}$  in the temperature range  $130^\circ$  to  $205^\circ\text{C}$ .<sup>5</sup> Midorikawa determined that NaCl made the largest contribution to the conductivity with the contribution from KCl being approximately one-half of that of NaCl. Thus small changes in the  $\text{AlCl}_3$  concentration would not significantly alter the conductivity of the eutectic. The eutectic is a good solvent for a large number of metal chlorides, oxides, and oxy-





chlorides.<sup>6,7,8,9</sup> The limiting reactions of the ternary eutectic require high potentials for discharge; chlorine evolution is the anodic limiting reaction, and 2.6 volts negative with respect to this reaction aluminum deposition occurs as the cathodic limiting reaction.

#### I-2. The Cd-CdCl<sub>2</sub> System

Magnetic susceptibility,<sup>10,11</sup> cryoscopic<sup>12</sup> and E.M.F. studies<sup>12,13,14</sup> for cadmium metal dissolved in molten CdCl<sub>2</sub> have been completed and indicate the existence of monovalent cadmium. Weidman's Law, which states that when a solution is formed from two or more components the gram susceptibility is ideally a linear combination of the specific susceptibilities of the pure components, was obeyed if Cd<sub>2</sub><sup>++</sup> was considered as the solute but not if Cd° was the solute. Solutions of Cd in CdCl<sub>2</sub> have been shown<sup>44</sup> to be diamagnetic which would eliminate the possibility of CdCl but not Cd<sub>2</sub>Cl<sub>2</sub>, metal atoms, or higher polymers. Cryoscopic experiments can also be explained by assuming that Cd° reacts with the halide to form a subhalide species. Slopes of plots of log of microequivalents of cathodic current versus EMF readings<sup>14</sup> had slopes corresponding to n=2 for Hg-HgCl<sub>2</sub>, Cd-CdCl<sub>2</sub> and Pb-PbI<sub>2</sub> (Table 1). The authors explained this value for the numbers of electrons involved



Table 1. Nernst n-Values in Divalent Metal-Metal  
Halide\* and Metal Halide - NaAlCl<sub>4</sub> Solution\*\*

System	Temp. ° C	Conc. Mole %	average corrected n value	precision of n value
Hg-HgCl <sub>2</sub>	287-297	≤0.3	2.02	0.01
Cd-CdCl <sub>2</sub>	578-581	≤0.3	2.04	0.04
Pb-PbI <sub>2</sub>	585-693	≤0.3	2.3	0.1
CdCl <sub>2</sub> -NaAlCl <sub>4</sub>	277	0.1-3.8	2.01	0.03
PbCl <sub>2</sub> -NaAlCl <sub>4</sub>	277	≤5.0	0.95	0.5
SnCl <sub>2</sub> -NaAlCl <sub>4</sub>	277	≤5.4	2.92	—

\* Taken from data by L. E. Topol, reference 13.

\*\* Taken from data by T. C. F. Munday and J. D. Corbett, reference 19.



by the equation  $2M^{+2} + 2e^- \rightleftharpoons M_2^{+2}$ . However, no attempt was made to distinguish the above reaction from the other possible electrochemical reaction  $M^{+2} + 2e^- \rightleftharpoons M^0$ .

### I-3. Acid Stabilization of Lower Valence States

If KCl is added to the Cd-CdCl<sub>2</sub> system less cadmium metal is dissolved.<sup>15</sup> Corbett and co-workers<sup>16</sup> explained this by a shift in the following equilibrium to the left because of the stronger interaction of the Cl<sup>-</sup> ion with the Cd<sup>++</sup> ion:  $(Cd^{++} + Cd^0 \rightleftharpoons Cd_2^{++})$ . Cubicciotti<sup>17</sup> has shown that if a strong chloride Lewis acid is added, the amount of reduction is significantly increased presumably by the greater interaction of Cl<sup>-</sup> with the acid. If the Cl<sup>-</sup> ion is tied up with the Lewis acid, it is no longer able to interact with the Cd(II) ion and the above equilibrium would be shifted to the right. This is the concept of acid stabilization<sup>18</sup> of lower valence states and the ternary eutectic used in this study should stabilize a lower valent state of cadmium ion with the tetrachloroaluminate (AlCl<sub>4</sub><sup>-</sup>) anion.

Stabilization of lower valence states will also occur as the halide size in a series of halides of a given element increases since the difference between the lattice energies of two different oxidation states is decreased by the larger halide if there is no change in





structure.<sup>19</sup> Therefore, if the familiar  $\text{Cl}^-$  anion of most chloride eutectics is replaced by the larger  $\text{AlCl}_4^-$  anion of this eutectic a smaller difference between the lattice energies of two oxidation states would be expected and the lower oxidation state would become more stable with respect to the higher state. The solid in the lower valence state would become more stable in this manner. However, the  $\text{AlCl}_4^-$  anion also stabilizes a lower valence cation in a melt by a smaller interaction with the higher valence cation since this anion has a lower charge density than a  $\text{Cl}^-$  anion. Steric effects would also be expected to favor the stabilization of a lower valence cation because of the difficulty in packing large  $\text{AlCl}_4^-$  anions around one cadmium ion. It has been shown<sup>18</sup> that when  $\text{AlCl}_4^-$  is the anion the amount of reduction of divalent cadmium to monovalent cadmium greatly increases over when  $\text{Cl}^-$  is the anion. (Table 2). The authors assumed that the solubility was attributable to  $\text{Cd}_2^{++}$ .

#### I-4. Solutions of $\text{CdCl}_2$ in Molten $\text{NaAlCl}_4$

E.M.F. measurements<sup>20</sup> for the reduction of dilute solutions of  $\text{CdCl}_2$  in molten 95%  $\text{NaAlCl}_4$ -5%  $\text{AlCl}_3$  indicated the existence of a monovalent cadmium species. (Table 1). The reduction product was identified as  $\text{Cd}_2^{++}$  which was distinguished from metal atoms and higher





allowed species such as  $\text{Cd}_3^{+4}$  and  $\text{Cd}_4^{+6}$ . It was previously thought that the subvalent species existed as the tri or tetraatomic cation<sup>12</sup> but these measurements were made in molten  $\text{CdCl}_2$  where the metal concentration was 5 to 10 mole % and where ideal behavior of the solute would be highly unlikely. Delimarskii<sup>21</sup> noted two inflections on a voltammogram of 5 mole %  $\text{CdCl}_2$  dissolved in equimolar  $\text{NaCl-AlCl}_3$  at  $300^\circ\text{C}$ . In a later paper<sup>22</sup> he explains the second inflection by the presence of cation complexes or cations with a different valence. However, he also observed a second wave when 5 mole %  $\text{NiCl}_2$ ,  $\text{CoCl}_2$  or  $\text{ZnCl}_2$  was the solute. Since multiple oxidation states would not be expected for all of these metals a continuation of this study would be desirable.

A Raman spectrum<sup>23</sup> of a mixture of doubly sublimed  $\text{CdCl}_2$  and  $\text{AlCl}_3$  heated to  $250^\circ\text{C}$  indicated the existence of  $\text{Cd}_2^{++}$  and the force constant of the dimer was calculated to be  $1.11 \text{ mdynes/\AA}$  which was compared to that of  $2.52 \text{ mdynes/\AA}$  for  $\text{Hg}_2^{++}$ . It was then concluded that instability of a monovalent cadmium compound relative to a monovalent mercury compound results from the relative magnitudes of the lattice energies of the compounds in the two oxidation states plus other fixed terms in the Born-Haber cycle including the sublimation energy of the metal, the ionization potential of the metal and the heat of



dissociation of the dimeric metal cation.

The Born-Haber cycle can also be used to qualitatively explain why  $\text{Cd}_2(\text{AlCl}_4)_2$  is a stable species while  $\text{Cd}_2\text{Cl}_2$  is not believed to exist since the cycle involving  $\text{Cd}_2(\text{AlCl}_4)_2$  contains more terms associated with the anion than the cycle involving  $\text{Cd}_2\text{Cl}_2$ . These additional terms could supply the extra energy required to stabilize the solid compound.

Yntema and co-workers<sup>6-9</sup> measured the deposition potentials of metal ions in this ternary eutectic but no attempt was made to identify the electrochemically active species. Polarographic studies<sup>24,25</sup> using a dropping mercury electrode have also been completed for several metallic cations in  $\text{AlCl}_3$ -metal chlorides ternary eutectics.

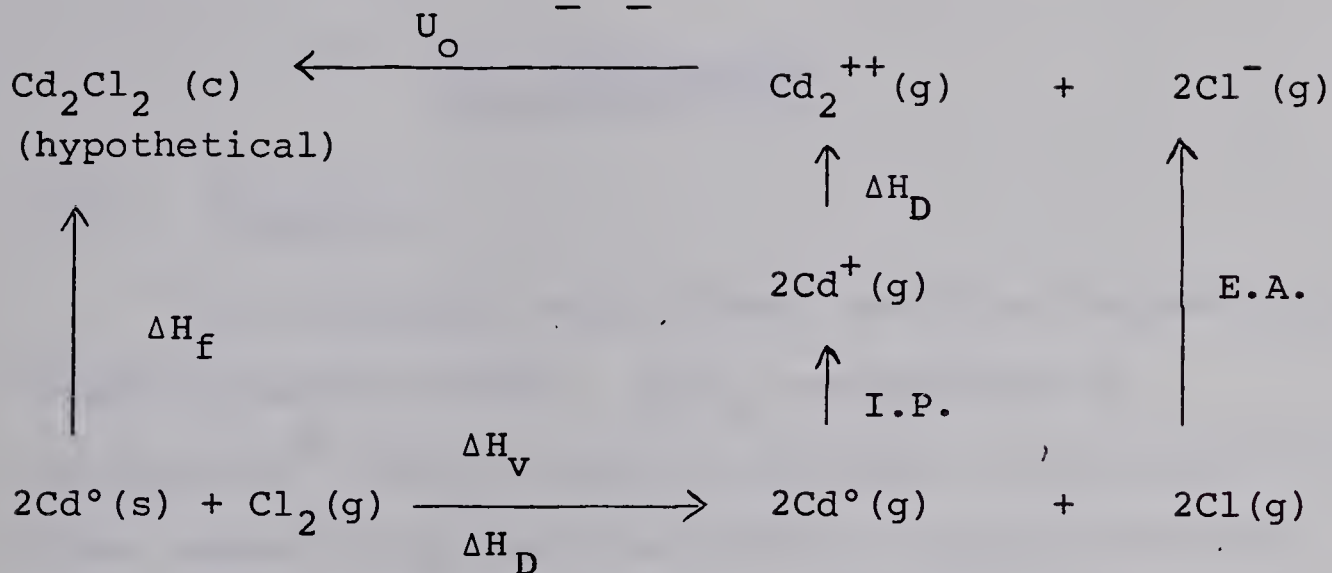
Table 2. Per Cent Reduction of  $\text{Cd}^{++}$  by  $\text{Cd}^\circ$  (liq.) In  
The Melts  $\text{CdX}_2$  and  $\text{CdX}_2-2\text{AlX}_3$

Halide	$\text{Cd}-\text{CdX}_2$ T°C	monoeutectic % reduction	$\text{Cd}-\text{Cd}(\text{AlX}_4)_2^*$ % reduction
$\text{CdCl}_2$	538	15.9	67.0
$\text{CdBr}_2$	536	16.4	57.5
$\text{CdI}_2$	383	2.6	31.2

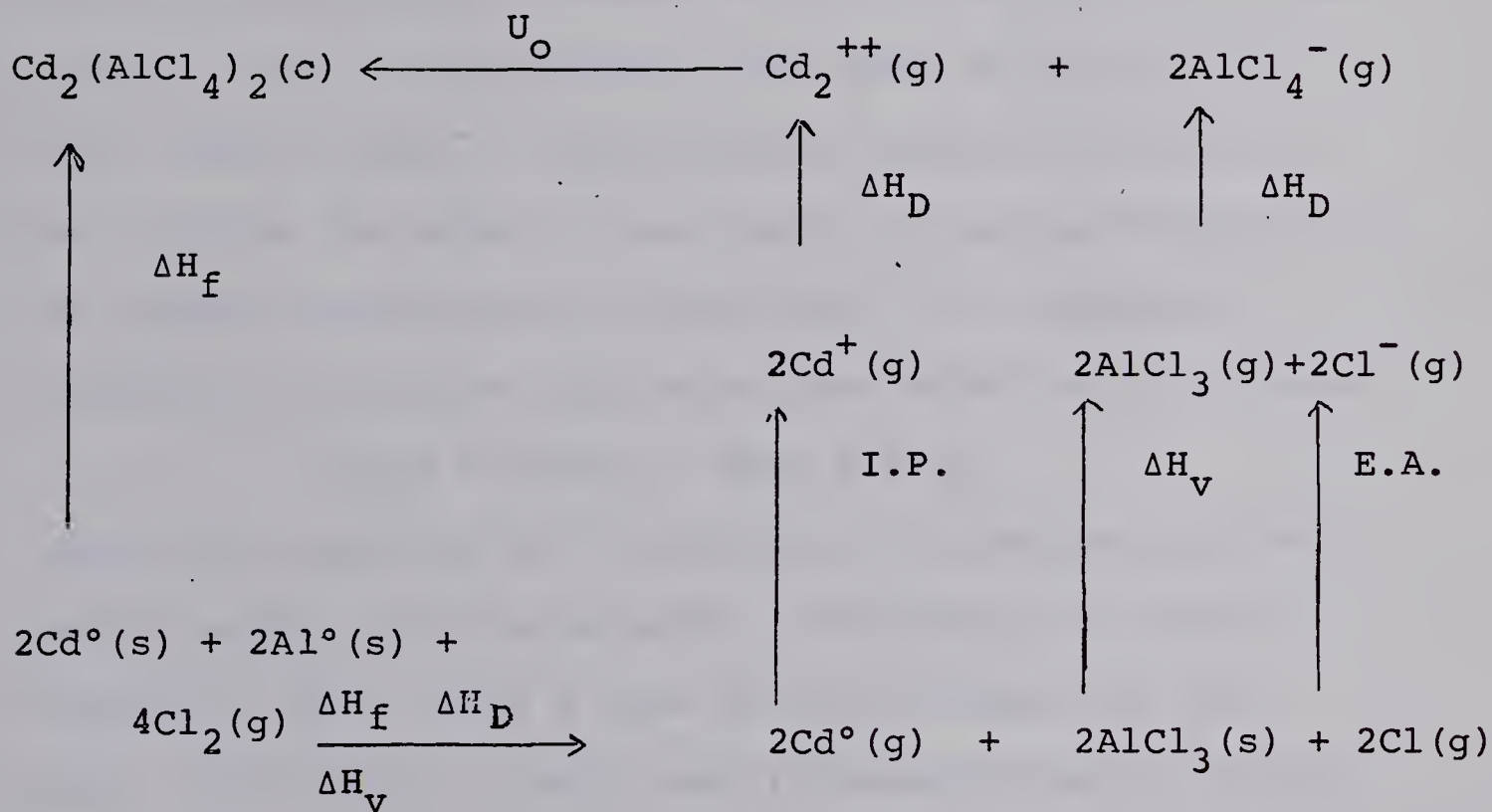
\* Temperature = 335°C for the  
reduction of  $\text{Cd}^{++}$  in  $\text{Cd}(\text{AlX}_4)_2$



Born-Haber Cycle for  $\text{Cd}_2\text{Cl}_2$



Born-Haber Cycle for  $\text{Cd}_2(\text{AlCl}_4)_2$



where

$U_o$  = lattice energy

$\Delta H_f$  = heat of formation

$\Delta H_V$  = heat of vaporization

$\Delta H_D$  = heat of dissociation

I.P. = first ionization potential

E.A. = electron affinity

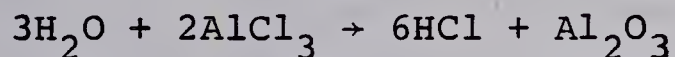




## II. EXPERIMENTAL

### II-1. Reagents

All chemicals were Fisher Certified Reagent grade unless otherwise stated.  $\text{AlCl}_3$  was purified by sublimation<sup>26</sup> under a positive pressure of nitrogen into a Pyrex vessel which could be tightly stoppered and then weighed. Aluminum metal turnings were added to the  $\text{AlCl}_3$  before sublimation to reduce the  $\text{FeCl}_3$  impurity to a non-volatile form.  $\text{NaCl}$  and  $\text{KCl}$  were dried by heating to  $350^\circ\text{C}$  under vacuum. The calculated amounts of  $\text{NaCl}$  and  $\text{KCl}$  to form the eutectic were added to the sublimed  $\text{AlCl}_3$ . To reduce contamination of the  $\text{AlCl}_3$  by atmospheric moisture an aluminum wire spiral was added to this vessel to



reduce the possible  $\text{HCl}$  contaminant to hydrogen gas which would escape from the eutectic. The vessel was then heated to  $200^\circ\text{C}$  under a flow of dry nitrogen for one hour. The molten eutectic was filtered through a 25-50  $\mu$  glass frit directly into the electrolytic cell. Further purification was effected by constant potential electrolysis (2.0 volts) between two large ( $2.0\text{ cm}^2$ ) platinum electrodes for several hours, during which time the current decreased by a factor of five.

$\text{ZnCl}_2$  and  $\text{CdCl}_2$ <sup>14</sup> were melted under a flow of





hydrogen chloride gas; after being molten for three hours, they were purged with nitrogen for one hour and finally filtered through a glass frit.  $\text{Hg}_2\text{Cl}_2$  was dried over  $\text{Mg}(\text{ClO}_4)_2$ . Reagent grade  $\text{HgCl}_2$  (Mallinckrodt) was purified by sublimation.

All material transfers were made in a nitrogen-filled glove box, but weighings were made on an analytical balance, which was located out of the box, using tightly stoppered weighing bottles. Moisture in the box was eliminated by passing the nitrogen over Linde Molecular Sieves (Union Carbide Corporation) and by storing open  $\text{P}_2\text{O}_5$  in the glove-box.

White heavy paraffin oil (Fisher, viscosity 335/350 USP) was circulated in an oil jacket surrounding the electrolytic cell (Figure 1) which was located in the glove box. A type NB-ELE constant temperature bath (Colora, West Germany) was used to maintain the oil temperature. Temperatures for various experimental runs varied from  $149^\circ\text{C}$  to  $159^\circ\text{C}$ , but the temperature was constant for each individual run to  $\pm 0.5^\circ\text{C}$ . The cell was closed with a machined Teflon stopper which had openings that allowed the electrodes to be inserted into the cell. Half-cells were isolated by glass tubes with 10-20 $\mu$  porosity glass fritted bottoms (Ace Glass Incorporated, Vineland, N.J.), when necessary. The chloride content of



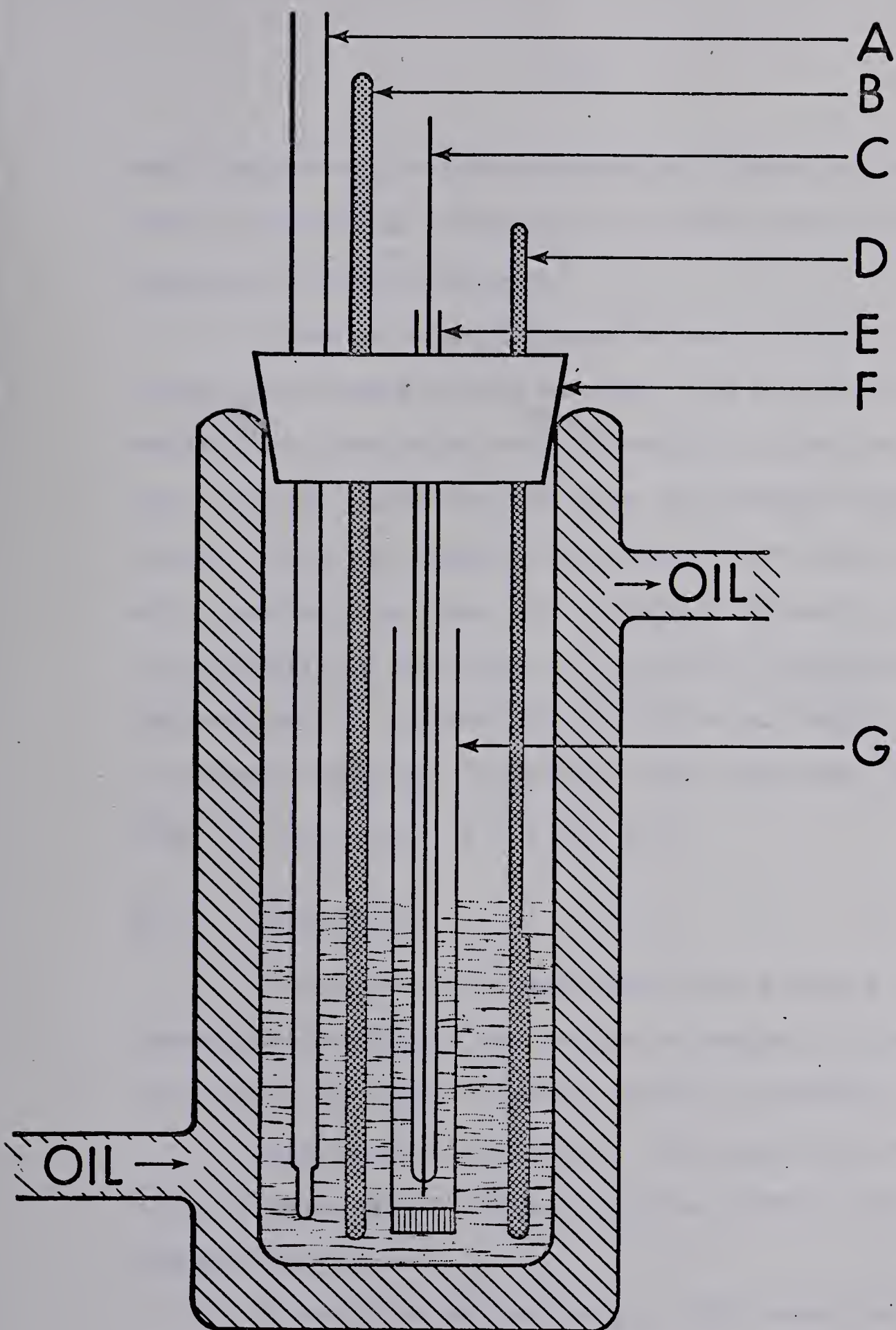


Figure 1. Electrolytic Cell. A, thermometer; B, aluminum counter electrode; C, tungsten wire; D, aluminum reference electrode; E, glass tube; F, Teflon stopper; G, fritted glass isolation compartment.



each compartment was determined by a Mohr titration which allowed the concentration of the metal ion in question to be calculated.

Tungsten and platinum indicator electrodes were found to be inert in the eutectic and were made by sealing the pure wire respectively into uranium and Pyrex glass tubing, allowing the wire to protrude beyond the glass. Zinc and cadmium electrodes were used in the pure wire form but the area was increased by bending the wire. An aluminum rod was used as the counter electrode for all determinations. A mercury electrode was made by inserting a tungsten wire into a mercury pool which was separated from the bulk melt by a glass frit.

## II-2. Apparatus

Potentials were measured with a Type K-3 potentiometer (Leeds and Northrup Company, Phila., Pa.) or a 3440A (Hewlett-Packard) digital voltmeter.

Coulometric oxidations and reductions were made using a Model IV Coulometric Current Source (E.H. Sargent and Co.).

A modified Anotrol Model 4100 potentiostat (Magna Electronics) was used for voltammetric scans and for constant potential electrolysis. A Model EUW-20A servo recorder (Heath) with a variable chart speed motor





was used for automatic recording of voltammetric scans.

Chronopotentiometric measurements employed a Model 6824A power supply/amplifier (Hewlett-Packard, Palo Alto, Calif.) in a constant current configuration controlled by appropriate mercury-wetted relay switching circuitry; measurements were recorded on a Hewlett-Packard Model 175A oscilloscope equipped with 1750B and 1781B plug in units and a Model 196B camera using ASA 3000 Polaroid film.

### II-3. The Al(III)/Al(O) Reference Electrode

An aluminum reference electrode has been established<sup>8,27,28</sup> using the Al(III)/Al(O) half-reaction and all potentials in this study were measured and are given with respect to this couple. However, the standard potential of the Ag(I)/Ag(O) couple was also determined so that potential values could be compared to those in other solvents. Although no generally accepted reference electrode is available for all molten salts, the subject of reference electrodes has been reviewed by Laity,<sup>29</sup> Delimarskii and Markov<sup>30</sup>, and Alabyshev, Lantratov, and Morachevskii.<sup>31</sup>

Reference electrodes reversible to metal ions are generally used in fused salts even though they have the disadvantage<sup>32</sup> of a potential being established at the





boundary of the two liquid phases. However, this effect is generally negligible in dilute solutions and electrodes of this type have the advantage of ease of preparation, good reproducibility, and reversibility.

If one is dealing with a solution and has defined the solvent to be in its standard state, the activity of the solvent is defined as unity. Since species in equilibrium with each other are of the same activity, the choice of a standard state for any species which is included in the solvent by a chemical equilibrium (i.e.  $\text{Cl}^-$  in molten alkali chlorides) cannot be independent of the choice of the solvent. Thus in a molten  $\text{AlCl}_3$ - $\text{NaCl}$ - $\text{KCl}$  eutectic the activity of  $\text{Al(III)}$  is equal to unity, and if a pure aluminum bar, whose activity is defined as unity following the usual thermodynamic convention, is immersed in the eutectic it will assume a fixed potential due to the  $\text{Al(III)}/\text{Al(0)}$  couple. This electrode would be expected to be unpolarizable since the change in concentration of  $\text{Al(III)}$  by the passage of anodic or cathodic electrical current would be negligible and the activity of  $\text{Al(0)}$  is fixed as unity. The non-polarizability of the aluminum electrode was determined in this study (Figure 2 ) by using a  $\text{Ag(I)}/\text{Ag(0)}$  reference electrode and varying the potential between the electrode in question and an aluminum counter electrode, and



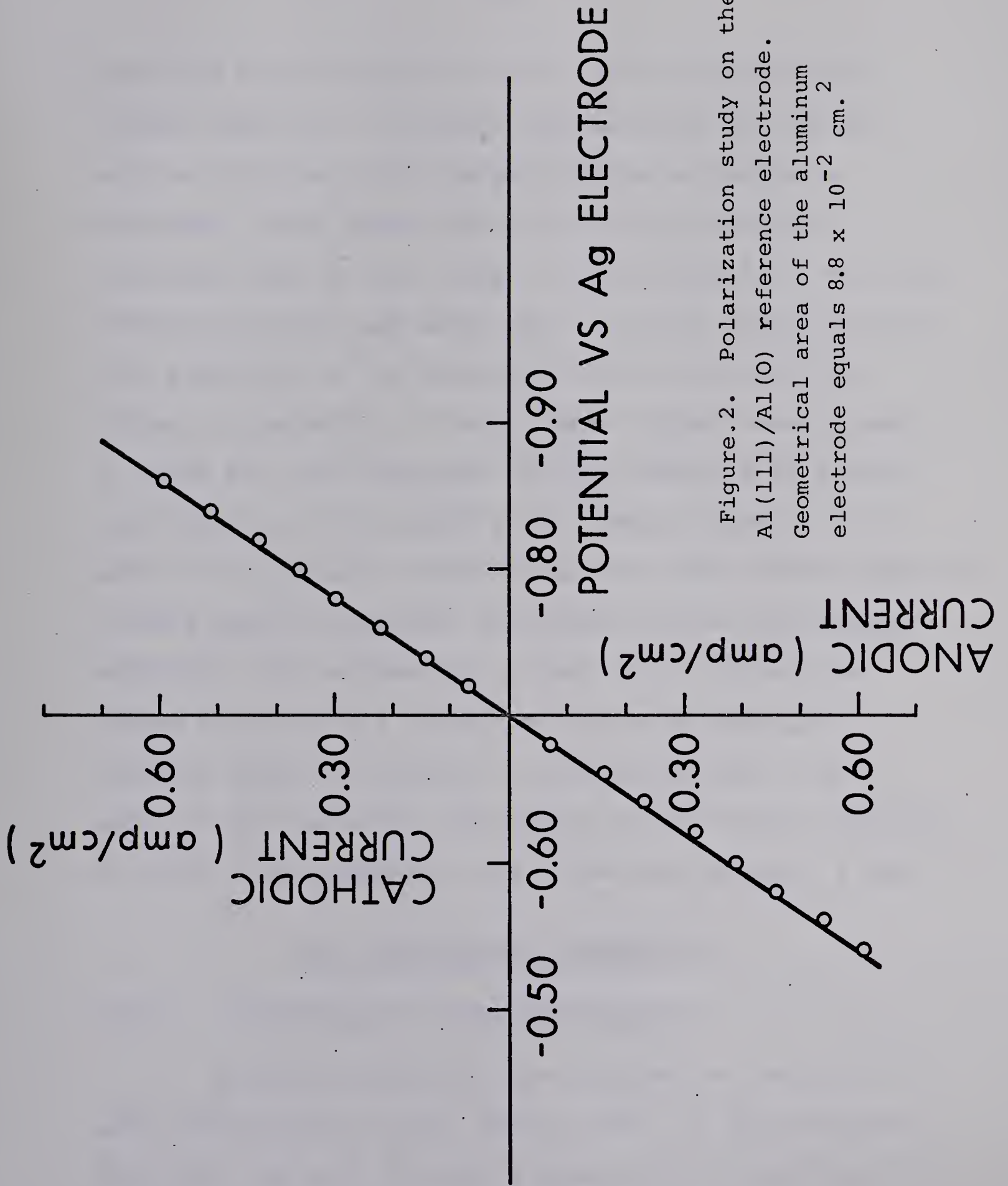


Figure.2. Polarization study on the Al(111)/Al(0) reference electrode. Geometrical area of the aluminum electrode equals  $8.8 \times 10^{-2} \text{ cm}^2$ .



measuring the resulting current. The current density-voltage curve was a straight line crossing the current axis at -0.70 volt with respect to the Ag reference electrode. This shows that the aluminum reference electrode used in this study is unpolarizable in the  $\text{AlCl}_3$ -NaCl-KCl eutectic and hence small currents passed through this electrode in the measurement of E.M.F. would not change its potential. The exchange current density must be large for this electrode and the reduction of  $\text{Al(III)}$  ions into it or the oxidation of aluminum metal from it must be a reversible process since the same current density-voltage graph is obtained regardless of the direction of scanning. The increase in current as the voltage is varied is due to the resistance of the electrolytic solution where the slope of a current-voltage graph is equal to the reciprocal resistance of the ternary eutectic at  $150^\circ\text{C}$ . The resistance was calculated to equal 3 ohms.

### III. RESULTS AND DISCUSSION

#### III-1. Electromotive Force Measurements

Standard potentials are reported on the basis of some concentration scale; molar, molal, or mole fraction. The molal and mole fraction scales have the advantage of not involving the density of the melt. However, standard potentials on the molar scale can be determined





by calculating the molarity using the formula  $d=a-bt$  where  $d=\text{gms/cc}$ ,  $t=^{\circ}\text{C}$ , and  $a$  and  $b$  are constants. The values of  $a$  and  $b$  were determined by Midorikawa<sup>33</sup> to be respectively 1.819 and  $8.77 \times 10^{-4}$  and the density was found to be linear over the temperature range 150-210°C. The potentials are measured in dilute solutions where Henry's Law is obeyed and the activity of the solute species is proportional to its concentration. If compartmented cells are used and the solute concentration is small the liquid junction potential across the porous glass frits will be sufficiently small that they can be neglected. However, this method of measuring potentials incorporates the Henry's Law constant for the solute into the value of the standard potential reported. For this reason potentials determined in this manner are generally taken at concentrations less than 0.1 molal where ideal behavior of the solute is maintained.

The I.U.P.A.C. Stockholm sign convention<sup>34</sup> is used throughout. All reductions unless otherwise stated were carried out at a current density of  $3.0 \text{ ma/cm}^2$ ; oxidations were carried out at approximately  $5.0 \text{ ma/cm}^2$ . The thermocouple effect was determined between all electrodes used and was found to be less than 0.0005 volt at 150°C. Since this is negligible no correction is necessary for the thermocouple effect. The quantity of





solute is negligible compared to the quantity of solvent in dilute solutions, and this assumption was made for the calculation of metal ion concentrations in this study. At least two separate determinations with a minimum of six experimental potential-concentration of electroactive species values per determination were made in calculating the standard potentials of the couples in question (See Table 3 for a sample of the method used in determining standard potential values). Standard potentials for all couples determined are given in Table 4.

If the  $\text{Zn}^{++}$  concentration was varied by oxidation of  $\text{Zn}^0$  or reduction of  $\text{ZnCl}_2$  the Nernst equation was obeyed and a two electron change was calculated ( $\text{Zn(II)} + 2e \rightleftharpoons \text{Zn(0)}$ ). Standard potentials on the molal, molar, and mole-fraction scales were calculated as the concentration of  $\text{Zn(II)}$  was varied by oxidation of  $\text{Zn(0)}$ .

Nernstian behavior was observed for the reduction of  $\text{HgCl}_2$  or the oxidation of  $\text{Hg}_2\text{Cl}_2$  with a two electron change being indicated per mole of  $\text{Hg}_2^{++}$ . The standard potential of the  $\text{Hg(II)}/\text{Hg(I)}$  couple was determined as  $\text{HgCl}_2$  was reduced to monovalent mercury ( $\text{Hg}_2^{++}$ ).

Similarly the Nernst equation was obeyed as a liquid mercury pool electrode was oxidized and the standard potential of the  $\text{Hg(I)}/\text{Hg(0)}$  couple was determined where monovalent mercury exists as the dimer ( $\text{Hg}_2^{++}$ ).



Table 3. Determination of the Standard Potential for the Hg(I)/Hg(O) Couple

generated moles Hg(I) $\times 10^5$	Concentration of Hg (I)			$-2.30RT/nF \log C$ where C			Experimentally Observed E.M.F.	$E_M^O$	$E_m^O$	$E_X^O$
	Molar(M) $\times 10^3$	Molal(m) $\times 10^3$	mole fraction (X) $\times 10^4$	<u>equals</u> Molar	Molal	mole fraction				
1.25	6.69	3.94	4.34	0.0908	0.100	0.140	0.935	1.026	1.035	1.075
2.50	13.4	7.89	8.68	0.0782	0.0878	0.128	0.950	1.028	1.038	1.078
3.75	20.0	11.8	13.0	0.0711	0.0806	0.119	0.958	1.029	1.039	1.077
5.00	26.8	15.7	17.4	0.0656	0.0754	0.115	0.962	1.028	1.037	1.077
7.50	40.0	23.7	26.0	0.0585	0.0679	0.108	0.969	1.028	1.037	1.077
10.0	53.5	31.5	34.7	0.0531	0.0627	0.103	0.974	1.027	1.037	1.077
12.5	66.9	39.4	43.4	0.0492	0.0587	0.0988	0.977	1.026	1.036	1.076
						mean standard potential		1.028	1.037	1.077

$E^O$  equals the standard potential at 423°K and the subscripts M, m, and X refer to the standard potentials on the molar, molal and mole fraction concentration scales.



Table 4. Electromotive Force Series In

Molten  $\text{AlCl}_3$ -NaCl-KCl at 423°K.

Couple	$E_M^O$ (v.)	$E_M^O$ (v.)	$E_X^O$ (v.)	Std. Dev. (v.)
$\text{Zn}^{++}/\text{Zn}^\circ$	0.254	0.263	0.304	0.002
$*\text{Cd}^{++}/\text{Cd}_2^{++}$	0.39	—	—	0.01
$*\text{Cd}_2^{++}/\text{Cd}^\circ$	0.27	—	—	0.01
$*\text{Cd}^{++}/\text{Cd}^\circ$	0.33	—	—	0.01
$\text{Ag}^+/\text{Ag}^\circ$	0.740	0.759	0.839	0.001
$\text{Hg}^{++}/\text{Hg}_2^{++}$	1.415	1.424	1.464	0.005
$\text{Hg}_2^{++}/\text{Hg}^\circ$	1.028	1.037	1.077	0.001
$\text{Hg}^{++}/\text{Hg}^\circ$	1.222	1.231	1.271	0.005

\*

These values are reported on the basis of  $E_{\tau/4}$  values.  
See Section III-3.





If the logarithm of one-half the equivalents of electricity used is plotted against potential as a  $\text{Cd}^\circ$  rod is oxidized a slope corresponding to a two electron change is observed. This oxidation could be explained if  $\text{Cd(II)}$  or if  $\text{Cd}_2^{++}(\text{Cd(I)})$  was the electrochemical reaction product. ( $\text{Cd(II)} + 2\text{e}^- \rightleftharpoons \text{Cd(0)}$ ) or  $\text{Cd}_2^{++} + 2\text{e}^- \rightleftharpoons \text{Cd(0)}$ ). The apparent standard potentials were calculated for these two couples by assuming that  $\text{Cd(II)}$  was the only reaction product in the first case and that  $\text{Cd}_2^{++}$  was the only product in the second case. The apparent standard potential on the molar, molal, and mole fraction scales for the first couple given is 0.336, 0.346, and 0.387 volt with a standard deviation of 0.003 volt; the apparent standard potential for the second couple on the same concentration scales is respectively 0.349, 0.359, 0.399 volt with a standard deviation of 0.003 volt.

However, if  $\text{CdCl}_2$  was added to the eutectic and reduced at a platinum or tungsten flag electrode no stable EMF values were obtained although the potential drift was followed for up to three hours. This behavior was observed regardless of whether the reduction was kept very small with respect to the  $\text{Cd(II)}$  concentration or whether it was a significant percentage of the  $\text{Cd(II)}$  concentrations. This was an unexpected observation since a previous study<sup>20</sup> reported the quantitative reduction of





Cd(II) to  $\text{Cd}_2^{++}$  where the  $\text{Cd}_2^{++}$  concentration was as high as 37% of the  $\text{Cd}^{++}$  concentration in a 95%  $\text{NaAlCl}_4$ -5%  $\text{AlCl}_3$  solvent at 277°C.

The values of the standard potentials obtained in this study are compared to an extrapolated standard potential in  $\text{AlCl}_3$ -NaCl-KCl given by Yntema<sup>8</sup> and to standard potentials in molten LiCl-KCl given by Laitinen.<sup>35</sup> Yntema's deposition potential values at 156°C for a one mole percent solution of the metal chloride were extrapolated using the Nernst equation and a standard potential value on the mole fraction scale is given (Table 5). Since dilute (1 mole percent) solutions were used the Nernst equation can be written as  $E = E_x^\circ + \frac{2.30RT}{nF} \log (0.01)$  where E equals the deposition potential measured by Yntema,  $E_x^\circ$  equals the standard potential based on the mole fraction scale, and where the other terms have their usual significance. This calculated  $E_x^\circ$  value is used in the above table for the deposition potentials reported by Yntema.

### III-2. Voltammetric Measurements

All voltammetric scans were taken using a tungsten cylindrical electrode with a geometrical area of  $1.2 \times 10^{-3} \text{ cm}^2$ . Scans were made from oxidizing to reducing potentials. The concentrations of the dissolved metal chlorides were



Table 5.

Comparison of Standard Potentials Obtained in this Study  
to Those by Yntema<sup>8</sup> and Laitinen<sup>35</sup>

Couple	This study $E_x^O$ 423°K in $AlCl_3-NaCl-KCl$	Yntema's Study $E_x^O$ 429°K in $AlCl_3-NaCl-KCl$	Laitinen's Study $E_x^O$ 723°K in $LiCl-KCl$
$*Al^{+++}/Al^o$	0.000	0.000	0.000
$Zn^{++}/Zn^o$	0.304	0.33	0.231
$Cd^{++}/Cd^o$	0.33**	0.45	0.481
$Ag^+/Ag^o$	0.839	0.83	1.160
$Hg_2^{++}/Hg^o$	1.077	1.0	—
$Hg^{++}/Hg_2^{++}$	1.464	1.2 (estimated)	—
$Hg^{++}/Hg_2^{++}$	1.271 (calc.)	1.1 (calc.)	1.3

\* The standard potentials are given with respect to an  $Al(111)Al(O)$  reference electrode whose standard potential is defined to be zero.

\*\* Calculated from experimental  $E_{\tau/4}$  values.



varied from 0.03 molal to 0.08 molal. (Figure 3).

If a voltammetric scan was taken of a solution of  $\text{ZnCl}_2$  one well defined wave was obtained indicating a single reduction which was shown by the E.M.F. measurements discussed above to involve two electrons per mole of  $\text{Zn(II)}$  consumed. This wave had a  $E_{1/2}$  value of 0.16 volt and it was shown to be diffusion controlled; the diffusion-limited current was directly proportional to concentration. If the  $\text{Zn(II)}$  concentration was reduced by coulometric reduction the only change in the voltammogram was a decrease in the height of the diffusion-limited plateau. This indicates that the divalent oxidation state of zinc is the only state present in this eutectic since formation of a sub-valent zinc ion would be expected to increase the anodic current prior to the cathodic wave.

A voltammogram of  $\text{HgCl}_2$  contained two waves with  $E_{1/2}$  values of +1.36 volts and +0.85 volt. This would correspond to the reduction of  $\text{Hg(II)}$  in two steps: the first to  $\text{Hg}_2^{++}$  and the second to  $\text{Hg(0)}$ . If the  $\text{Hg(II)}$  concentration was reduced coulometrically the height of both diffusion-limited plateaus decreased linearly as expected and there was an increase in the anodic current prior to the first reduction wave.

If a voltammogram of a dilute solution of  $\text{CdCl}_2$  was taken two waves were obtained. The first wave was a very small ill-defined wave (it caused a significant





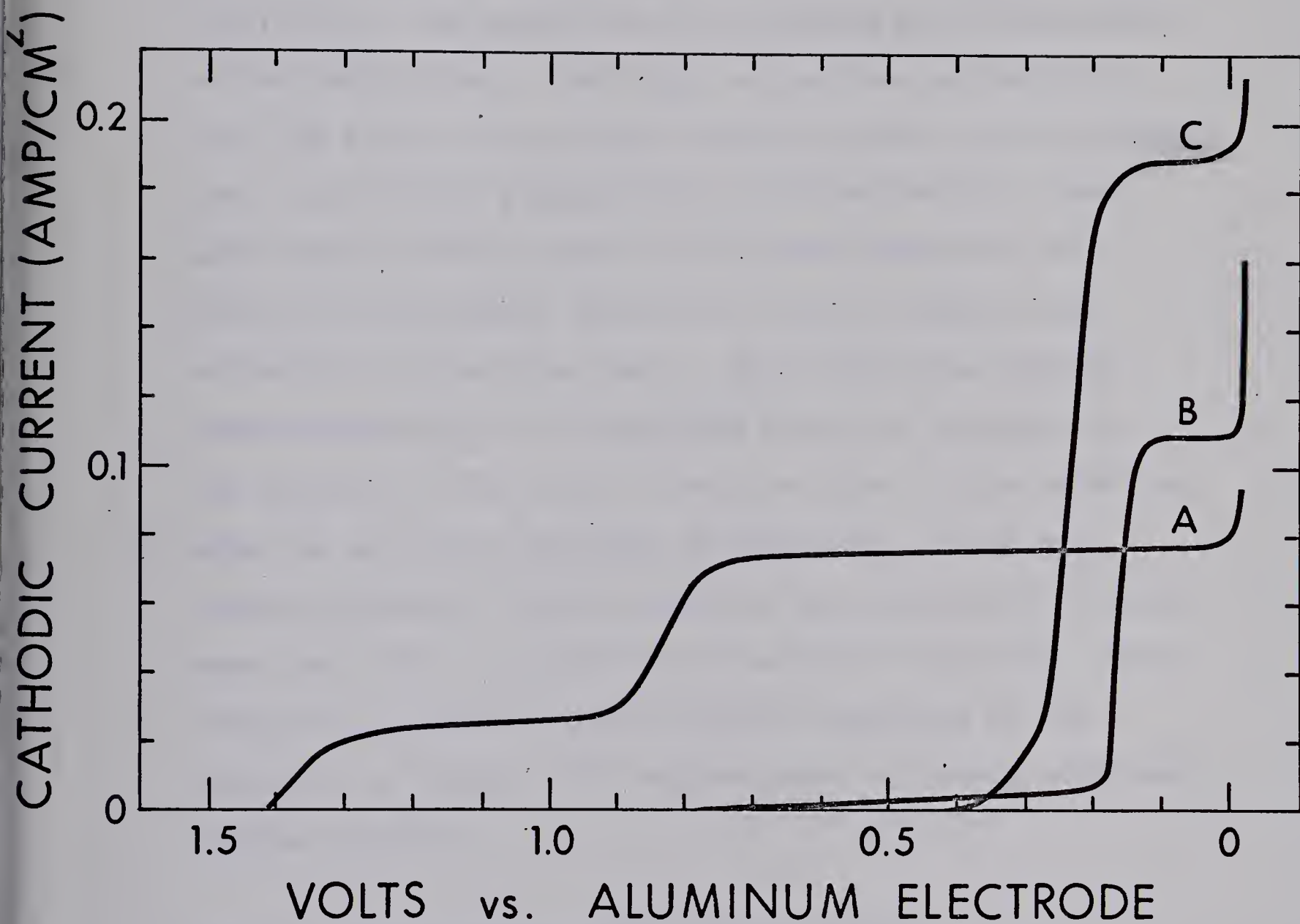


Figure 3. Voltammetric scans for solutions of metal chlorides in molten  $\text{AlCl}_3\text{-NaCl-KCl}$  at  $150^\circ\text{C}$ . A, 0.03 molal  $\text{HgCl}_2$ ; B, 0.04 molal  $\text{ZnCl}_2$ ; C, 0.05 molal  $\text{CdCl}_2$ .





rounding at the start of the second wave) and is believed to correspond to the first step in the reduction  $\text{Cd(II)}/\text{Cd(I)}/\text{Cd(0)}$ ; the second was well defined and corresponded to the second step. The  $E_{1/2}$  values were approximately +0.3 and +0.22 volt and the limiting current for the second wave was directly proportional to concentration. Long scan times of three hours per volt and reduction of  $\text{Cd(II)}$  at low current densities failed to improve the definition of the first wave. When  $\text{Cd(II)}$  was reduced electrochemically a voltammogram showed an increase in the current in the anodic direction prior to the reduction wave, as well as a decrease in the height of the well defined plateau. Similar behavior was observed if cadmium metal was left in contact with the  $\text{Cd(II)}$  solution. This increase in anodic current could be explained by the reduction of  $\text{Cd(II)}$  with cadmium metal to form a subvalent cadmium species.

### III-3. Chronopotentiometric Measurements

In chronopotentiometry the current through an electrochemical cell is kept constant. The potential of the indicator electrode changes with time due to the changing concentration of the electroactive species at its surface, and this changing potential is recorded as a function of time. The electrode potential changes



markedly when concentration polarization occurs and the concentration of the reactant at the electrode surface decreases to zero. Finally the change is sufficient to allow another reaction to occur, thus stabilizing the potential.

The transition time is defined as the time required for complete concentration polarization. Sand proposed the equation<sup>36</sup>

$$\tau^{1/2} = \frac{\pi^{1/2} n F A D^{1/2} C}{2i}$$

where  $\tau$  = Transition time (seconds)

A = Electrode area (cm<sup>2</sup>)

D = Diffusion coefficient (cm<sup>2</sup>/sec)

C = Concentration (moles/cm<sup>3</sup>)

i = Current (amps)

n = Faradays per molar unit of reaction

F = Faraday (96,493 coulombs)

$\pi$  = 3.1416

This equation holds regardless of the reversibility or irreversibility of the electrode reaction. A more complete theoretical description of chronopotentiometry can be found in several recent reviews on the subject.<sup>37,38</sup>

Several methods have been proposed for measuring transition times.<sup>39-42</sup> The method of Reinmuth<sup>40</sup> was



chosen for all chronopotentiograms in this study since it was better suited for the determination of transition times from a chronopotentiogram containing two separate transitions.

A tungsten cylindrical electrode whose geometrical area was  $1.6 \times 10^{-2} \text{ cm}^2$  was used as the indicator electrode for all chronopotentiometric experiments. The chronopotentiometer was initially used to pass anodic current through the cell, then three minutes were allowed for the solution to become quiescent and finally the chronopotentiometer was used to pass cathodic current through the cell and the reduction wave was recorded.

Chronopotentiometric experiments on a solution of Zn(II) (whether added as the salt or coulometrically) were obtained where one well-defined transition was observed (Figure 4). If the current was reversed during this transition one transition was obtained in the oxidation direction in which  $\tau_{\text{red}}$  was approximately equal to  $\tau_{\text{ox}}$ . This would correspond to the plating of a metal on the electrode.<sup>43</sup>

If the Sand equation is obeyed,  $\tau^{1/2}$  should be proportional to  $A/i$  for identical concentrations. Thus if  $\log \tau$  is plotted against  $\log i$  a straight line of slope minus two should be observed. Slopes of  $-2.0 \pm 0.1$  were obtained for all determinations. A plot of  $\tau^{1/2}/C$





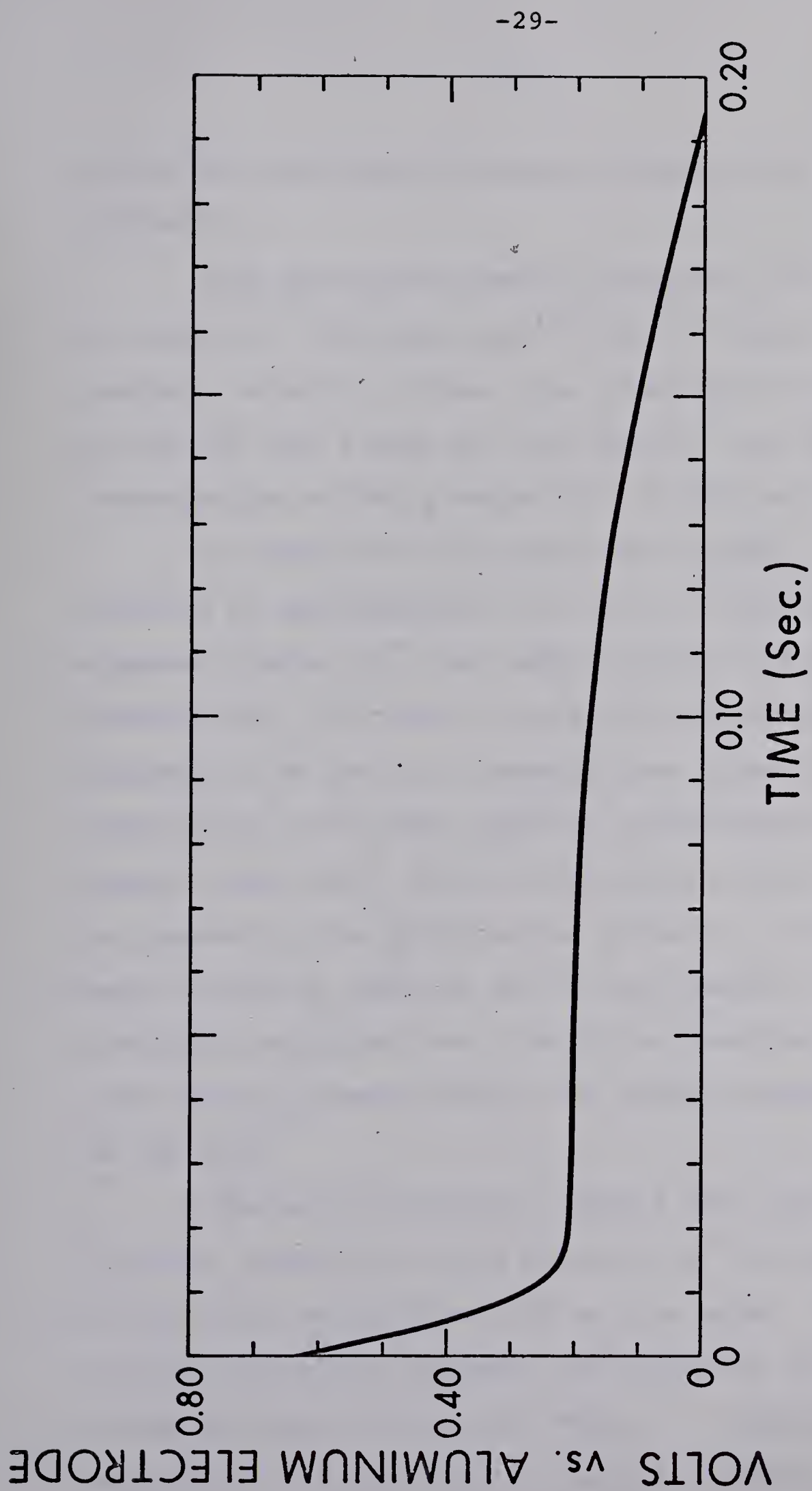


Figure 4. Chronopotentiogram of 0.06 molal  $\text{ZnCl}_2$  in molten  $\text{AlCl}_3$ - $\text{NaCl}$ - $\text{KCl}$  at  $150^\circ\text{C}$ . Current equals 6.50 milliamps.



versus the reciprocal of current density gave a straight line (Figure 5).

The chronopotentiometric constant ( $i\tau^{1/2}/C$ ) was equal to 0.0325 amp sec<sup>1/2</sup> molal<sup>-1</sup> with a relative standard deviation of less than 4% as the current density was varied from 0.0625 to 0.100 amp cm<sup>2</sup> and as the concentration of ZnCl<sub>2</sub> varied from 0.0643 to 0.144 molal.

In addition to the main wave a small inflection appeared at approximately +0.4 volts. This inflection appeared whether Zn<sup>++</sup> was added coulometrically or whether ZnCl<sub>2</sub> was added; it was not well defined and is believed to be due to a trace of some impurity. An oxychloride is the main impurity (approximately 2.5%) in reagent grade ZnCl<sub>2</sub> and it is possible that all of it was not removed in the purification procedure. Since Zn<sup>0</sup> metal is easily oxidized and it was immersed in a melt containing chloride ions it would be possible to get the same impurity whether Zn(II) was added coulometrically or as the salt.

Chronopotentiometric results were also obtained for CdCl<sub>2</sub> dissolved in the eutectic as the concentration of CdCl<sub>2</sub> was varied from 0.01 to 0.04 molal. Two well-defined transitions appeared (A, Figure 6) with  $E_{\tau/4}$  values of 0.39 volt and 0.27 volt. This small separation in  $E_{\tau/4}$  potentials made it difficult to obtain



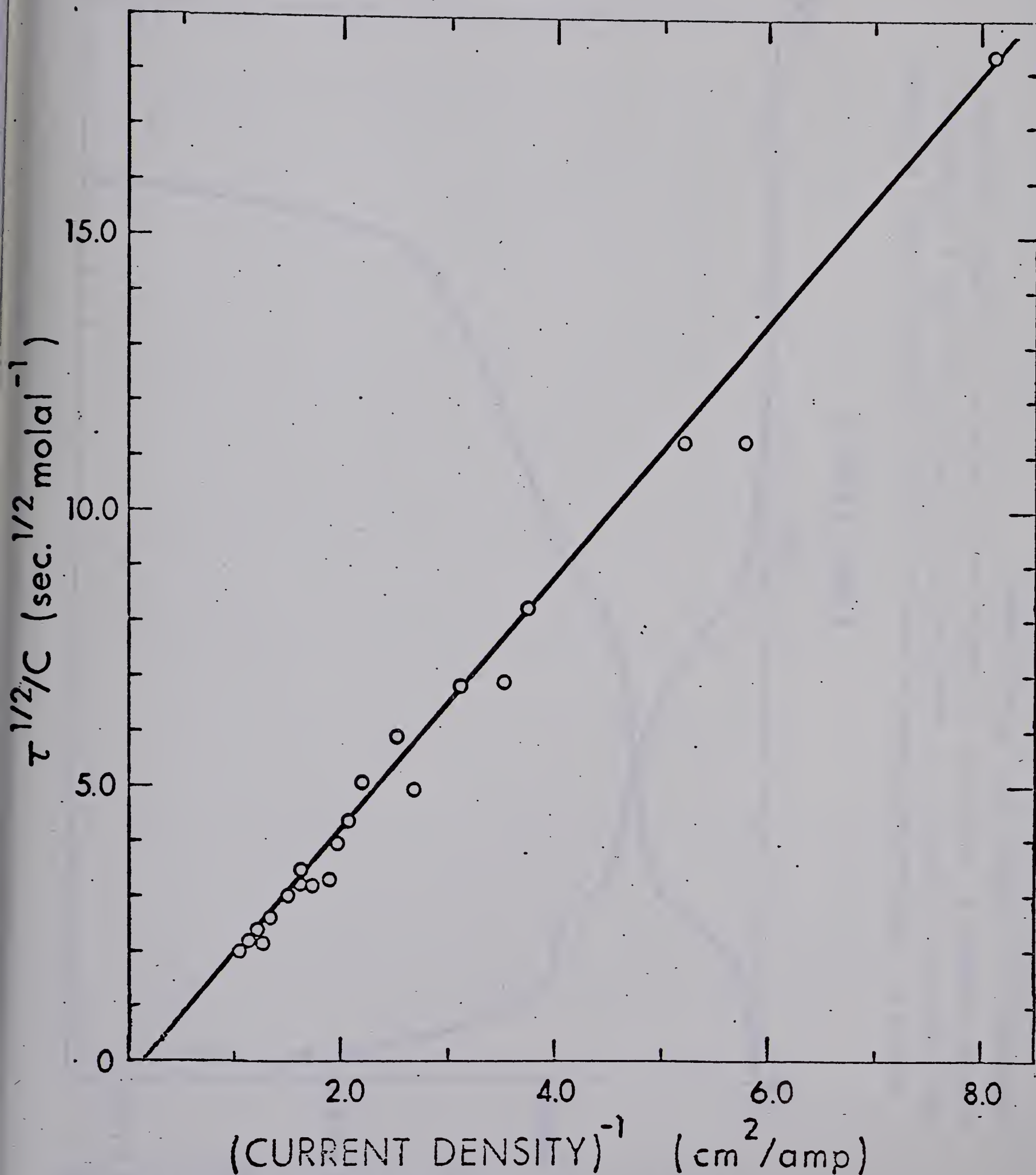


Figure 5.  $\tau^{1/2}/C$  versus the reciprocal of current density for dilute solutions of  $\text{ZnCl}_2$  in molten  $\text{AlCl}_3\text{-NaCl-KCl}$  at  $150^\circ\text{C}$ .



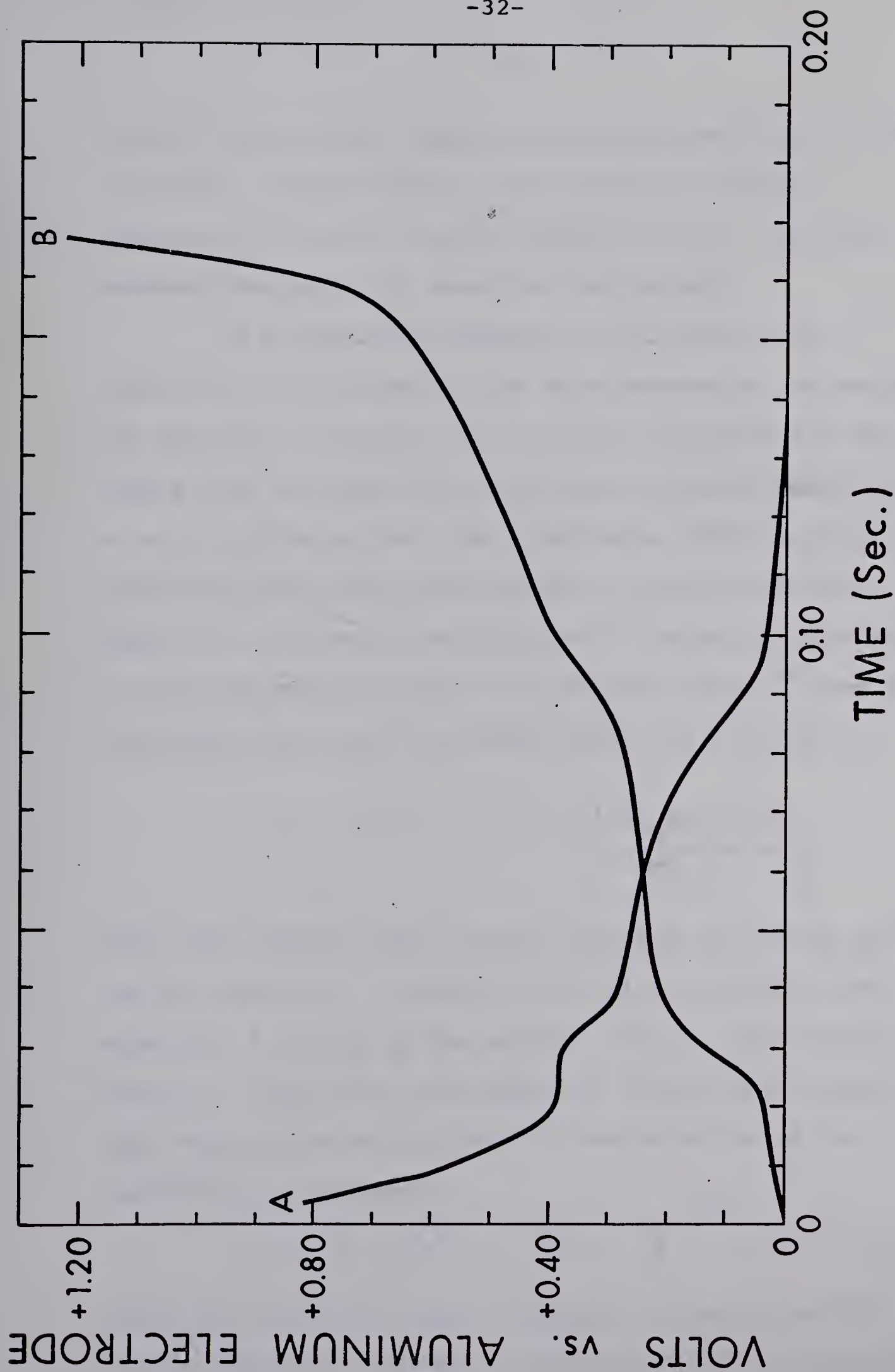


Figure 6. Chronopotentiometric scans for dilute solutions of  $\text{CdCl}_2$  in molten  $\text{AlCl}_3\text{-NaCl-KCl}$  at  $150^\circ\text{C}$ . A, reduction of 0.03 molal  $\text{CdCl}_2$  with a current of 5.00 milliamps; B, oxidation of cadmium metal plated on a tungsten indicator electrode at a current of 2.78 milliamps.





results over a large range of current densities, but once a suitable current density was determined several chronopotentiograms could be obtained with a relative standard deviation of less than one percent.

If a substance undergoes a multiple stage reduction or oxidation two or more successive inflections are observed. However, the current efficiency for the second step is less than 100% since the first substance is still diffusing into the electrode. This results in the transition time being longer for the second step than for a solution containing only the second substance at the same concentration. It has been shown<sup>44</sup> that the transition time for the second substance is given by

$$(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} = \frac{\pi^{1/2} n_2 F A D_2^{1/2} C_2}{2 i}$$

where the symbols have the same meaning as already defined and the subscript 1 refers to the first substance and the subscript 2 refers to the second. Thus a relationship between  $\tau$  values and the number of electrons involved in each step can be established by manipulation of the preceding two equations:

$$(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} = \frac{n_2 \tau_1^{1/2}}{n_1} \quad \text{since } D_1 = D_2,$$

and  $C_1 = C_2$  for the two stage oxidation or reduction of a single substance through a stable intermediate species. This



can be arranged to the more familiar form:<sup>45</sup>

$$\frac{\tau_2}{\tau_1} = \frac{2n_2}{n_1} + \left(\frac{n_2}{n_1}\right)^2$$

Therefore if  $n_2=n_1$  as is expected for the Cd(II)/Cd(I)/Cd(0) system  $\tau_2$  should equal  $3\tau_1$ . The experimental value of  $\tau_2/\tau_1$  was  $3.0 \pm 0.3$  over the current range used. The value of  $\tau^{1/2}$  is proportional to the reciprocal of current if the concentration of the electroactive species at the electrode is constant and if the indicator electrode area does not change. The proportionality constant is  $\frac{\pi^{1/2} n F A D^{1/2} C}{2}$  where the symbols have the same significance as defined earlier. Thus if  $\log \tau$  is plotted versus  $\log i$  a straight line with a slope of -2.0 should be observed. Plots of  $\log \tau$  versus  $\log i$  gave slopes of  $-2.0 \pm 0.2$  for both transitions. The chronopotentiometric constants were constant (Table 6) for both transitions for different concentrations of Cd(II) and a plot of  $\tau^{1/2}/C$  versus the reciprocal of current density gave a straight line for both transitions (Figure 7).

Two transitions were observed for the oxidation of cadmium metal which had previously been plated onto a platinum electrode (Figure 6, B). This would agree with the results obtained when  $\text{CdCl}_2$  was reduced through an



Table 6.

Chronopotentiometric Results for Solutions of  $\text{CdCl}_2$  in  $\text{AlCl}_3$ - $\text{NaCl}$ - $\text{KCl}$  at  $150^\circ\text{C}$ 

Concentration molal	$\tau_1$ seconds	$\tau_2$ seconds	$\tau_2/\tau_1$	current ma	amp sec $\tau_1^{1/2}/\text{C}$	amp sec $\tau_2^{1/2}/\text{C}$	amp sec $\tau_2^{1/2}/\text{C}$
0.0246	0.0070	0.0212	3.0	6.22	0.0211		0.0369
0.0246	0.0067	0.0203	3.0	6.22	0.0207		0.0359
0.0246	0.0066	0.0192	2.9	6.22	0.0205		0.0351
0.0246	0.0112	0.0354	3.2	5.00	0.0215		0.0382
0.0246	0.0106	0.0344	3.3	5.00	0.0209		0.0378
0.0246	0.0150	0.0486	3.2	4.00	0.0199		0.0358
0.0138	0.0300	0.0885	3.0	1.75	0.0219		0.0377
0.0138	0.0136	0.0434	3.2	2.46	0.0208		0.0371
0.0138	0.0106	0.0346	3.3	2.79	0.0201		0.0376
0.0138	0.0195	0.0580	3.0	1.99	0.0201		0.0348
0.0138	0.0210	0.0615	2.9	3.46	0.0230		0.0393





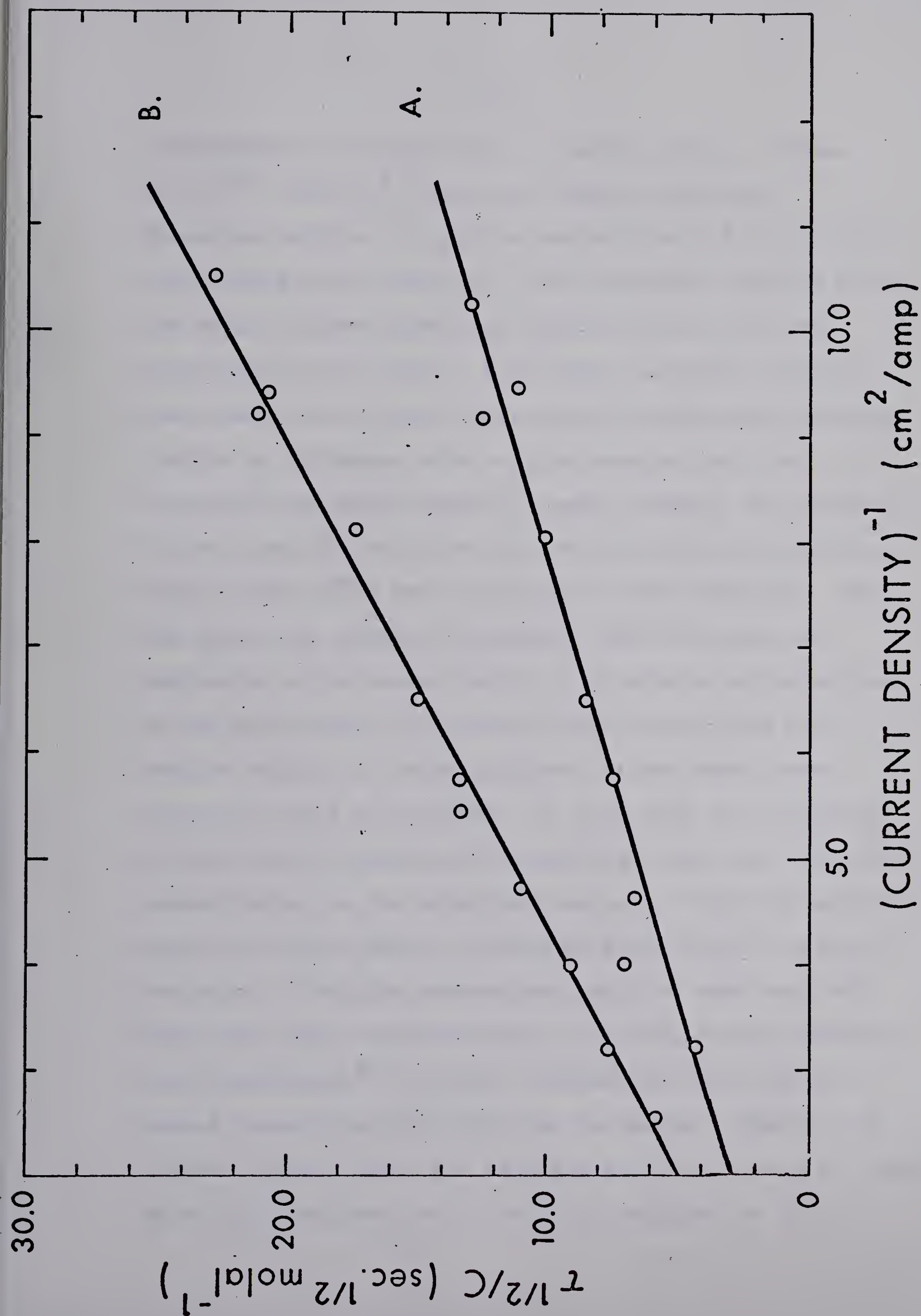


Figure 7.  $\tau^{1/2}/C$  versus the reciprocal of current density for the chronopotentiometric reduction of dilute solutions of CdCl<sub>2</sub> in molten AlCl<sub>3</sub>-NaCl-KCl at 150°C. A, the Cd<sup>++</sup>/Cd<sub>2</sub><sup>++</sup> transition; B, the Cd<sub>2</sub><sup>++</sup>/Cd<sup>++</sup> transition.



intermediate univalent state to cadmium metal. Values of  $i\tau_1^{1/2}$  and  $i\tau_2^{1/2}$  were not constant for this oxidation and the  $\tau_2/\tau_1$  ratio varied from 1.0 to 2.0 with the average value being 1.4. This would be expected since the weight of the deposit of cadmium on the indicator electrode was not known. Since the transition time for the oxidation of a metal plated onto an electrode is not limited by diffusion of a soluble species into the electrode but by the amount of metal present, the potential of the electrode would be only able to change slightly as long as oxidizable metal remained on the electrode. When the metal was completely oxidized (this situation is analogous to the concentration of a soluble ion being zero at the electrode) the potential would change and the species capable of being oxidized at the next lowest potential would be oxidized. In this case the oxidation of Cd(I) would stabilize the potential rise until the Cd(I) concentration at the electrode was zero. Then the potential would rise again until it would be stabilized by chlorine evolution. Thus two transitions would be observed, but since the first transition was not controlled by diffusion the relationship<sup>44</sup>  $\tau_2/\tau_1=3$  between the first and the second transition time would not be obeyed. However, if all the cadmium metal was oxidized to Cd(I), the Cd(I) would be at the electrode and it would be oxidized to Cd(II).



Therefore the second transition time would be expected to equal the transition time for the first step in the oxidation if none of the  $\text{Cd(I)}$  diffused away from the electrode. However, the second transition time was experimentally observed to be larger than the first transition time which can be explained if the concentration of  $\text{Cd(I)}$  at the electrode is larger than expected. There are two reasons for the concentration of  $\text{Cd(I)}$  to be larger than expected. The primary reason is the reaction of the  $\text{Cd(II)}$  that diffuses into the electrode with metallic cadmium at the electrode to produce  $\text{Cd(I)}$ . A secondary effect accounting for a larger  $\tau_2$  value would result because of the small initial concentration of  $\text{Cd(I)}$  in solution. This initial small concentration of  $\text{Cd(I)}$  would retard the diffusion of the chronopotentiometric generated univalent cadmium away from the electrode and thus increase the  $\text{Cd(I)}$  concentration at the electrode. A larger influence from the  $\text{Cd(I)}$  concentration would be expected when cadmium metal was oxidized than when  $\text{CdCl}_2$  was reduced because of the larger quantity of cadmium metal present in the former case which would react with  $\text{Cd(II)}$ . If current reversal chronopotentiometry is used,





first plating metal on the electrode and then oxidizing it off, the transition time for the oxidation of metal is less than the transition time required to plate it on. This effect is observed for the deposition of cadmium and aluminum from a dilute solution of  $\text{CdCl}_2$ , and for the deposition of mercury and aluminum from a dilute solution of  $\text{HgCl}_2$ . The smaller transition time corresponds to less metal present than is expected, and in the case of cadmium and mercury would be caused by the reaction of the plus two ion with the corresponding metal to yield monovalent metal ion. The quantity of aluminum would be less than expected since it would reduce the  $\text{Cd(II)}$  present in the  $\text{CdCl}_2$  solution, and the  $\text{Hg(II)}$  present in the  $\text{HgCl}_2$  solution, and in the process would be oxidized to aluminum ion.

$E_{\tau/4}$  for a particular couple is related to the standard potential for that couple and it has been shown<sup>46</sup> that

$$E_{\tau/4} = E^\circ + \frac{RT}{nF} \ln \frac{f_o D_r^{1/2}}{f_r D_o^{1/2}}$$

where  $E^\circ$  equals the standard potential (volts),  $D$  equals the diffusion coefficient ( $\text{cm}^2/\text{sec}$ ),  $f$  equals the activity coefficient,  $r$  refers to the reductant,  $o$  refers





to the oxidant,  $R$  equals 8.314 joules/deg. mole,  $T$  equals absolute temperature,  $F$  equals the Faraday (96,493 coulombs), and  $n$  equals the Faradays per molar unit of reaction. Since the  $f_o D_r^{1/2} / f_r D_o^{1/2}$  term is expected to be close to unity,  $E_{\tau/4}$  values are approximately equal to standard potential values and the equilibrium constant for  $\text{Cd}^{++} + \text{Cd}^\circ \rightleftharpoons \text{Cd}_2^{++}$  at 150°C was calculated to equal 26 by using  $E_{\tau/4}$  values for the  $\text{Cd}^{++} / \text{Cd}_2^{++}$  and  $\text{Cd}_2^{++} / \text{Cd}^\circ$  couples.

The equilibrium constant for the analogous reaction of mercury with  $\text{Hg(II)}$  at the same temperature was calculated to be  $3.6 \times 10^4$  using the standard potential values for the  $\text{Hg(II)}/\text{Hg(I)}$  and  $\text{Hg(I)}/\text{Hg(0)}$  couples determined in this study. A similar value was obtained if  $E_{\tau/4}$  values were used. This equilibrium constant is much larger than the one in water at 25°C,  $1.1 \times 10^2$ , calculated by using tabulated values for the half reactions involved.<sup>47</sup> These increased equilibrium constants in  $\text{AlCl}_3\text{-NaCl-KCl}$  illustrate that monovalent mercury and cadmium are more stable in this eutectic than in water, thus

indicating the stabilization of lower valence states by this eutectic.

If  $\text{HgCl}_2$  was added to the eutectic and reduced chronopotentiometrically two transitions were noted with  $E_{\tau/4}$  values of +1.3 volts and +0.93 volt (Figure 8) which



VOLTS vs. ALUMINUM ELECTRODE

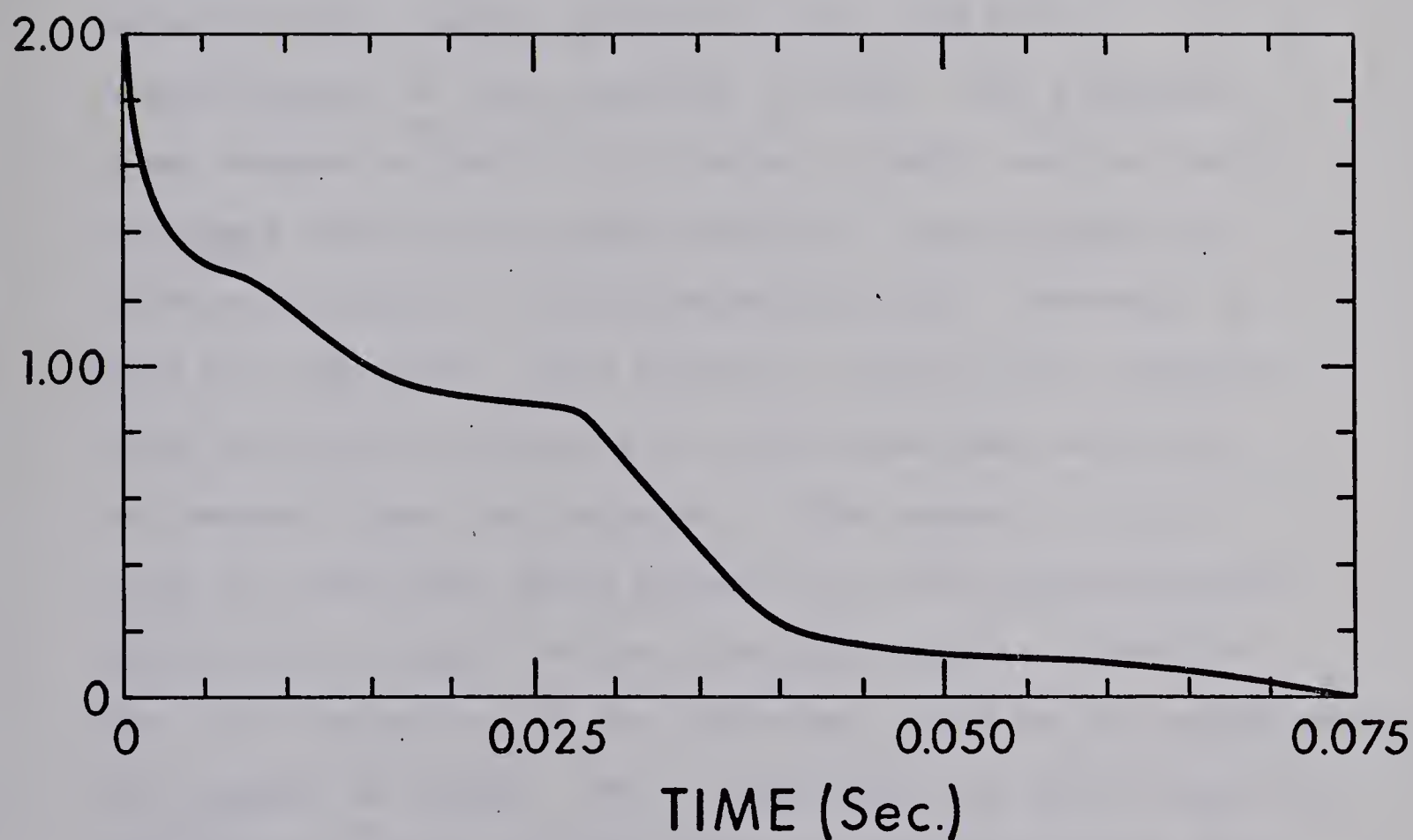


Figure 8. Chronopotentiogram for 0.03 molal  $\text{HgCl}_2$  in molten  $\text{AlCl}_3$ - $\text{NaCl}$ - $\text{KCl}$  at  $150^\circ\text{C}$ . Current equals 12.5 milliamps.



would correspond to the  $\text{Hg(II)}/\text{Hg(I)}$  and  $\text{Hg(I)}/\text{Hg(O)}$  half-reactions. However, the  $\tau_2/\tau_1$  ratio varied between one and three and the  $i \tau_1^{1/2}/C$  and  $i \tau_2^{1/2}/C$  ratios were not constant. This anomalous behavior can be explained since the  $\text{Hg(O)}$  produced in the chronopotentiometric reduction of  $\text{HgCl}_2$  would react quantitatively with  $\text{Hg(II)}$  to produce  $\text{Hg(I)}$ . During the plateau of the first transition the ratio of  $\text{Hg(II)}$  concentration to  $\text{Hg(I)}$  concentration changes gradually until the  $\text{Hg(II)}$  concentration at the electrode is zero. The potential then changes and  $\text{Hg(I)}$  is reduced to  $\text{Hg(O)}$  and the ratio of these activities should gradually change producing another plateau on the chronopotentiogram. However, in this case the  $\text{Hg(O)}$  would undergo a quantitative reaction with the  $\text{Hg(II)}$  diffusing into the electrode and would be removed from the electrode. This removal of  $\text{Hg(O)}$  from the electrode would compete with the electrochemical production of  $\text{Hg(O)}$  on the electrode and the transition for the second step in the reduction would not be established as rapidly as normal. This competition for  $\text{Hg(O)}$  would be expected to give a sloping region between the first and second transitions (Figure 8) which was experimentally observed. This distortion of the chronopotentiograms for dilute solutions of  $\text{HgCl}_2$  made it extremely difficult to precisely define the end of the first transition and





the start of the next. Thus transition times varied greatly depending on the method of measurement. This distortion is more pronounced for the reduction of  $\text{HgCl}_2$  than for the reduction of  $\text{CdCl}_2$  because of the large difference in equilibrium constants favoring lower valence states. The bulk concentration of  $\text{Hg(I)}$  during the chronopotentiometric reduction of  $\text{HgCl}_2$  would be much larger than the bulk concentration of  $\text{Cd(I)}$  during the chronopotentiometric reduction of  $\text{CdCl}_2$  due to the relative magnitudes of the equilibrium constants. This bulk concentration of  $\text{Hg(I)}$  would also cause the  $\tau_2/\tau_1$  ratio to vary from the theoretical value of three while the similar distortion of a chronopotentiogram of a  $\text{CdCl}_2$  solution, caused by the small concentration of  $\text{Cd(I)}$ , would be much smaller. This effect must be small for the cadmium system as evidenced by the average  $\tau_2/\tau_1$  value of 3.09 with a standard deviation of 0.15. This standard deviation compares favorably with the standard deviation of 0.11 (average equalled 2.97) obtained by Berzins and Delahay<sup>44</sup> for the stepwise reduction of oxygen in water.

Diffusion coefficients were calculated for  $\text{Zn(II)}$ ,  $\text{Cd(II)}$  and  $\text{Cd(I)}$  from the slopes of plots of  $\tau^{1/2}/C$  versus the reciprocal of current density (Figures 4 and 6). The value for  $\text{Cd(II)}$  and  $\text{Cd(I)}$  is  $1.8 \times 10^{-5} \text{ cm}^2/\text{sec}$  at  $150^\circ\text{C}$  and the value for  $\text{Zn(II)}$  is  $6.5 \times 10^{-5}$



$\text{cm}^2 \text{sec}^{-1}$  at this temperature. These values are in reasonable agreement with those for  $\text{Cd(II)}$  and  $\text{Zn(II)}$  in molten  $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$  at  $160^\circ$  which were determined by the less accurate voltammetric<sup>48</sup> method to be  $1.5 \times 10^{-6} \text{ cm}^2 \text{sec}^{-1}$ . The diffusion coefficient for  $\text{Cd(II)}$  is in excellent agreement with the value determined from chronopotentiometric data<sup>49</sup> in molten  $\text{LiCl-KCl}$  at  $450^\circ \text{C}$ . to be  $1.7 \times 10^{-5} \text{ cm}^2 \text{sec}^{-1}$  and from voltammetric data<sup>50</sup> at  $500^\circ \text{C}$  to be  $2.7 \times 10^{-5} \text{ cm}^2 \text{sec}^{-1}$ .

The potentiometry experiments can be explained using the equilibrium constants calculated above. The oxidation of a mercury pool or the reduction of a  $\text{HgCl}_2$  solution proceeded without complication because the equilibrium constant favors the quantitative formation of  $\text{Hg(I)}$ .

However, the equilibrium constant does not quantitatively favor the formation of  $\text{Cd(I)}$ . When a cadmium rod is anodized the product is primarily  $\text{Cd(I)}$  but since the generation will not be quantitative some  $\text{Cd(II)}$  will also be formed. Thus, although stable E.M.F. values were obtained, the Nernst equation contains the equilibrium constant relating the concentrations of  $\text{Cd(I)}$  and  $\text{Cd(II)}$  and the apparent standard potential obtained will not necessarily be associated with only one cadmium couple. If  $\text{CdCl}_2$  is reduced, the reduction to



Cd(I) will proceed but if the concentration of Cd(I) in the vicinity of the electrode becomes high there will be disproportionation into Cd(II) and Cd(0); the Cd metal will remain on the electrode. Stable potentials will not be obtained thereafter since the diffusion of Cd(II) towards the electrode will result in generation of more Cd(I) which must then diffuse away. This process will continue until the supply of Cd metal on the electrode is exhausted. The concentrations of Cd(II), Cd(I), and Cd(0) changing at the electrode surface will give rise to a potential drift, as observed.

A similar problem of mixed oxidation states was encountered during the oxidation of Nb(0) in molten LiCl-KCl.<sup>51</sup> A reaction product mixture of Nb(IV) and Nb(III) was obtained and the approximate concentration ratio of Nb(IV)/Nb(III) was three.

The oxidation of Zr(0) in molten LiCl-KCl is more complicated since the reaction products depend on the temperature during the oxidation.<sup>52</sup> Zr(II) was the product at 550°C while Zr (IV) was produced at 450°C. Standard potential values at 450°C based on the mole fraction scale were given for the Zr(II)/Zr(0) couple (extrapolated from 550°C) and the Zr(IV)/Zr(0) couple to be -1.75 volts and -1.86 volts with respect to a platinum reference electrode. The Zr(IV)/Zr(II) potential was





calculated to equal -1.97 volts with respect to the same reference and there is 0.22 volt difference from the  $\text{Zr(II)}/\text{Zr(0)}$  potential. Mixed oxidation states can be expected to occur when there is a small separation in the potentials of successive oxidation states. Thus this complication of mixed oxidation potentials is not limited to one solvent but occurs whenever the potentials are very close to one another.

#### 4. CONCLUSION

The electroanalytical techniques of potentiometry, voltammetry, and chronopotentiometry were used to study dilute solutions of the Group IIB metal ions in molten  $\text{AlCl}_3\text{-NaCl-KCl}$ . Zinc was shown to exist in the plus two oxidation state while cadmium and mercury were shown to exist in both the plus one and plus two oxidation states. The technique of chronopotentiometry was especially applicable in the study of the cadmium system since it verified the reversibility of the  $\text{Cd(II)}/\text{Cd(I)}$  and the  $\text{Cd(I)}/\text{Cd(0)}$  couples and it allowed the diffusion coefficient to be calculated for  $\text{Cd(II)}$ . Since the  $\tau_2/\tau_1$  ratio was obeyed the diffusion coefficient of  $\text{Cd(I)}$  would be approximately equal to that of  $\text{Cd(II)}$ . The diffusion coefficient was also calculated for  $\text{Zn(II)}$ .





A partial standard potential series was obtained which should be very useful for further work in the  $\text{AlCl}_3$ - $\text{NaCl}$ - $\text{KCl}$  eutectic. Equilibrium constants calculated from  $E_{\tau/4}$  values were shown to be approximately equal to those calculated from standard potential values and equilibrium constants were calculated for the reaction of the higher valence species of cadmium and mercury with their respective metals to yield lower valence species. The equilibrium constants favored the monovalent mercury species more than the monovalent cadmium species. These values for the equilibrium constants explained some apparent anomalies in the electrochemistry of cadmium and mercury.



BIBLIOGRAPHY

1. J. A. Plambeck, J. Chem. Eng. Data, 12, 77 (1967).
2. V. A. Plotnikov and U. I. Shvartsman, Mem. Inst. Chem. Acad. Sci. Ukrain. SSR, 387 (1936), CA 31, 6093<sup>1</sup>.
3. L. Wasilewski, A. Kaezorowski and M. Dynken, Prgemsyl Chem. 18, 608 (1934).
4. R. Midorikawa, J. Electrochem. Soc. Japan, 23, 352 (1955).
5. R. Midorikawa, J. Electrochem. Soc. Japan, 24, 83 (1956).
6. W. H. Wade, G. O. Twellmeyer, and L. F. Yntema, Trans. Electrochem. Soc. 78, 77 (1940).
7. E. Marshall and L. F. Yntema, J. Phys. Chem. 46, 353 (1942).
8. R. G. Verdieck and L. F. Yntema, J. Phys. Chem. 46, 344 (1942).
9. R. Wehrman and L. F. Yntema, J. Phys. Chem. 48, 259 (1944); 48, 268 (1944).
10. N. H. Nachtrieb, J. Phys. Chem. 66, 1163 (1962).
11. J. Farquharson and E. Heymann, Trans. Faraday Soc. 311, 1004 (1935).
12. L. E. Topol and A. L. Landis, J. Am. Chem. Soc. 82, 6291 (1960).



13. M. Okado, K. Yoshida, and Y. Hisamatsu, J. Electrochem. Soc. Japan, 32, 99 (1964).
14. L. E. Topol, J. Phys. Chem. 67, 2222 (1963).
15. K. Grjotheim, F. Gronvold, and J. Krogh-Moe, J. Am. Chem. Soc. 77, 5824 (1955).
16. J. D. Corbett, S. V. Winbush and F. C. Albers, J. Am. Chem. Soc. 79, 3020 (1957).
17. D. Cubicciotti, J. Am. Chem. Soc. 74, 1198 (1952).
18. J. D. Corbett, W. J. Burkhard, and L. F. Druding, J. Am. Chem. Soc. 83, 76 (1961).
19. A. Van Arkel, Research 2, 307 (1949).
20. T. F. Munday and J. D. Corbett, Inorg. Chem. 5, 1263 (1966).
21. Iu. K. Delimarskii, E. M. Skobets, and L. S. Berenblyum, Zhur. Fiz. Khim. 22, 1108 (1948), CA 43, 8915e.
22. Iu. K. Delimarskii, L. S. Berenblyum, and I. N. Sheiko, Zhur. Fiz. Khim. 25, 398 (1951), CA 45, 8378f.
23. J. D. Corbett, Inorg. Chem. 1, 700 (1962).
24. R. Martin de Fremont, R. Rosset, and M. Leroy, Bull. Soc. Chim. France, 706 (1964).
25. M. Saito, S. Suzuki, and H. Goto, J. Chem. Soc. Japan, Pure Chem. 83, 883 (1962).
26. E. D. Perry, Private Communication.
27. V. A. Plotnikov, E. J. Kirichenko, and N. S. Fortunatov, Zapiski Inst. Khim. Akad. Nauk. U.R.S.R. 7, 159 (1940), CA 35, 3530<sup>8</sup>.





28. A. M. Skundin, V. Sh. Palanker, and V. S. Bagotskii, *Elektro Kimiya*. 2, 1458 (1966), CA 66, 51657 q.
29. R. W. Laity. "Reference Electrodes: Theory and Practice", edited by D. G. Ives and G. J. Janz, Academic Press, New York (1961).
30. Iu. K. Delimarskii, and B. F. Markov. "Electrochemistry of Fused Salts", translated by A. Peiperl, edited by R. E. Wood, Sigma Press, Washington, D.C. (1961).
31. A. F. Alabyshev, M. F. Lantratov, and A. G. Morachevskii. "Reference Electrodes for Fused Salts", translated by A. Peiperl, Sigma Press, Washington, D. C. (1965).
32. A. F. Alabyshev, M. F. Lantratov, and A. G. Morachevskii, "Reference Electrodes for Fused Salts", translated by A. Peiperl, Sigma Press, Washington, D.C. (1965) p. 117.
33. R. Midorikawa, *J. Electrochem. Soc. Japan*, 23, 352 (1955).
34. H. A. Laitinen, "Chemical Analysis", McGraw-Hill Book Company Inc., New York (1960) p. 276.
35. H. A. Laitinen and C. H. Liu, *J. Am. Chem. Soc.* 80, 1015 (1958).
36. A. J. S. Sand, *Phil. Mag.* 1, 45 (1901).
37. P. Delahay, "New Instrumental Methods In Electrochemistry", Interscience Publishers Inc., New York (1966) p. 179.



38. A. J. Bard, "Electroanalytical Chemistry", Volume 1, Marcel Dekker Inc. New York (1966) p. 157.
39. P. Delahay and C. Mattax, J. Am. Chem. Soc. 76, 874 (1954).
40. W. H. Reinmuth, Anal. Chem. 33, 485 (1961).
41. C. D. Russel and J. M. Peterson, J. Electroanal. Chem. 5, 467 (1963).
42. D. G. Peters and S. L. Burden, Anal. Chem. 38, 530 (1966).
43. A. J. Bard, "Electroanalytical Chemistry", Volume 1, Marcel Dekker Inc. New York (1966), p. 169.
44. T. Berzins and P. Delahay, J. Am. Chem. Soc., 75, 4205 (1953).
45. P. Delahay, "New Instrumental Methods In Electrochemistry", Interscience Publishers, Inc., New York (1966) p. 192.
46. A. J. Bard, "Electroanalytical Chemistry", Volume 1, Marcel Dekker Inc., New York (1966) p. 161.
47. W. M. Latimer, "Oxidation Potentials", 2nd edition, Prentice Hall, Inc. Englewood Cliffs, N. J. (1952).
48. M. Steinberg and N. Nachtrieb, J. Am. Chem. Soc. 72, 3558 (1950).
49. H. A. Laitinen and W. S. Ferguson, Anal. Chem. 29, 4 (1957).



50. P. Drossbach and P. Petrick, Z. Electrochem. 58, 95 (1954).
51. R. D. Caton, Jr. and H. Freund, Anal. Chem. 36, 15 (1964).
52. R. Baboian, D. Hill, and R. Bailey, J. Electrochem. Soc. 112, 1221 (1965).











**B29882**